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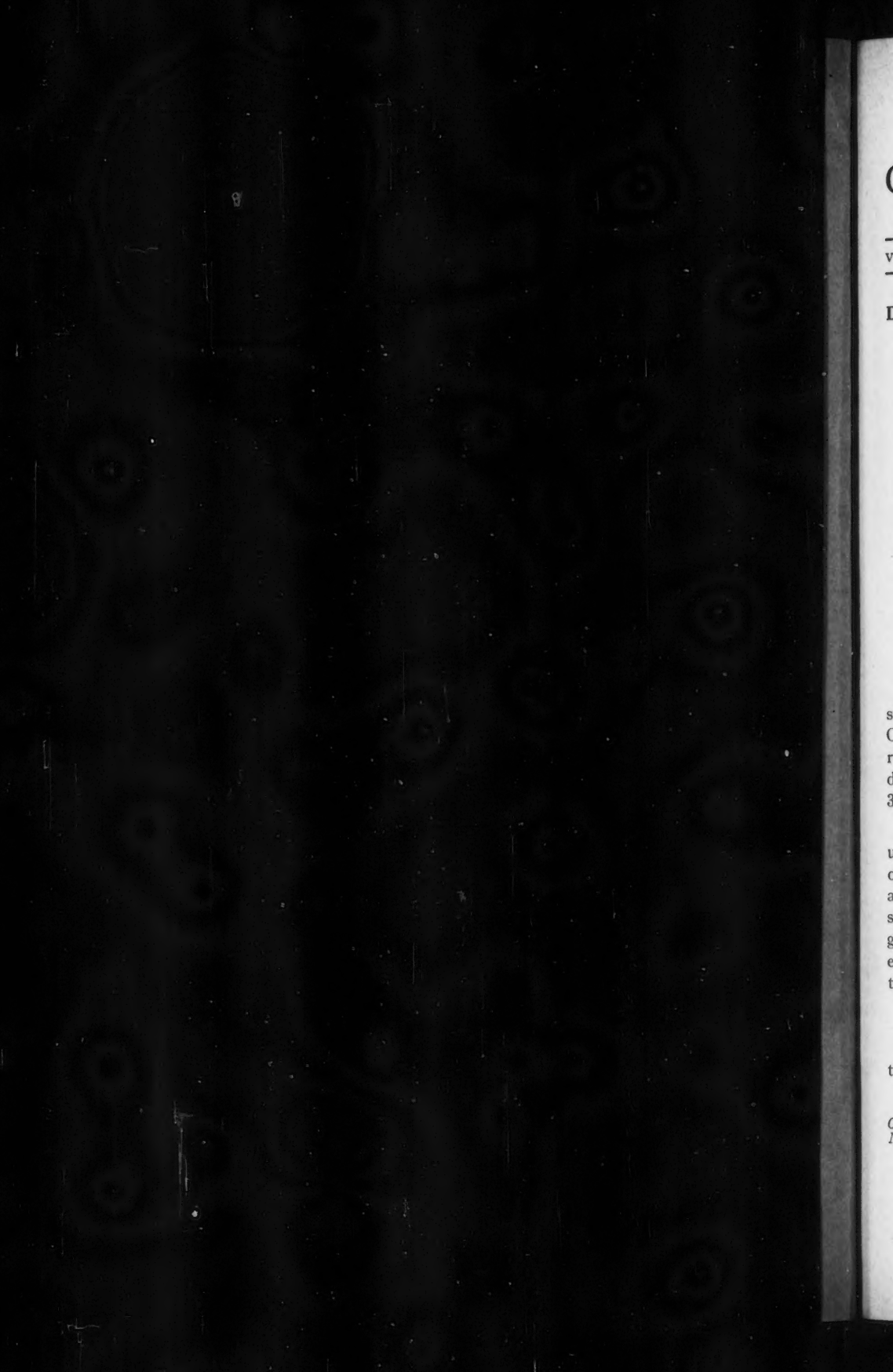
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# Canadian Journal of Technology

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## DEPLETION OF CARBOHYDRATE RESERVES BY STARVATION AND EXERCISE<sup>1</sup>

BY DYSON ROSE AND RUTH PETERSON

### Abstract

Experiments with rats showed that reserve carbohydrate in both muscle and liver was somewhat depleted by starvation and was seriously depleted by exercise. A combination of these two caused maximum depletion. Negligible recovery of these reserves occurred in 24 hr. when starvation was continued, but recovery was complete within six hours when sugar was fed, and after 12 hr. the level exceeded that found in untreated control animals. Experiments with hogs indicated that recovery of muscle carbohydrate reserves occurred in about eight hours following feeding of a high sugar food. Feeding of oat chop alone, or chop and molasses, was less efficacious than feeding chop and sugar. These experiments indicate that current methods of handling hogs at the slaughter house result in low glycogen reserves and the meat produced will therefore have an undesirably high pH. Feeding of a mixture of sugar and chop immediately upon receipt of the animal at the plant would alleviate this condition.

### Introduction

Recent studies on meat products have emphasized the influence of pre-slaughter treatment of the animal on the quality of meat produced (3, 4, 7, 8). One of the factors controlling the quality of meat is the level of carbohydrate reserve present in muscles when circulation ceases, and this reserve is directly dependent upon the treatment received by the animal during the last 20 to 30 hr. before slaughter.

As previously noted (7), Canadian hogs are highly variable and it is difficult, using them as test animals, to obtain consistent and reliable results in studies of the effect of small variations in preslaughter treatments. Laboratory animals, such as albino rats, are more tractable for such experiments, and it seems reasonable to assume that results obtained with these animals will be generally applicable to larger domestic species. Experimental tests of the effects of starvation and fatigue on hogs, and of recovery following such treatments, were therefore supplemented with similar tests on rats.

### Materials and Methods

For some tests young male rats were purchased\* and assigned at random to the various treatments, for others, pregnant females were purchased and the

<sup>1</sup> Manuscript received May 7, 1951.

Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as paper No. 265 of the Canadian Committee on Food Preservation and as N.R.C. No. 2506.

\* From the Charles River Breeding Laboratories, Boston.

young used. Young of only one sex were used in any one experiment. All rats were given a diet of prepared "Checkers" and raised under as uniform conditions as possible.

Rats that were to be fatigued by exercise were trained to run in a motor driven race 13 in. in diameter. Training was accomplished by subjecting the rats to exercise twice daily over a 30 day period; during this period the speed of rotation of the race was gradually increased from 6 to 15 r.p.m., and the running time from 5 to 15 min. Twice daily exercise at 15 r.p.m. for 15 min. was then continued until the day before slaughter.

The rats were stunned by a sharp blow and immediately decapitated. The two principal lobes of the liver were removed at once, weighed, and placed in 30% potassium hydroxide solution. The hind legs, and usually one fore leg, were removed, skinned, and placed in sample bottles at 30° F. (- 1.1° C.) overnight to allow decomposition of glycogen to lactic acid (1, 6). The flesh of the legs was then trimmed off and used for the determination of lactic acid (hind legs) and of pH (fore leg).

All hogs used were obtained at a local packing plant, and their history is unknown. Slaughtering and processing methods were those in common use at such plants, except that psoas muscles were removed from the carcass before it was taken to the chilling rooms.

Glycogen was determined in the hydroxide digest of the livers by an anthrone method (9), the two lobes of the liver being analyzed individually and considered as duplicates. The combined weight of these two lobes was recorded as liver "weight". Lactic acid was determined by the *p*-hydroxy diphenyl method of Barker and Summerson (2) in a trichloroacetic acid extract obtained by grinding the muscles with sand in a mortar. Left and right legs were treated as duplicates. The pH was determined in muscle brei as suggested by Callow (5).

## Results

### *Relative Effects of Starvation and Exercise on Rats*

Two tests were conducted with rats to determine the relative effects of starvation and exercise on the carbohydrate reserve and to determine the severity of treatment required to deplete these reserves in the trained animals. All animals were rested for 24 hr. before being subjected to the experimental preslaughter treatment shown in Table I.

Table I presents the results, as averages of the five rats used in each treatment, for both trials. In Trial II the variance within treatments of the liver glycogen content and muscle pH was significantly altered by the imposed experimental treatment of the animals, and an over-all necessary difference for significance could not be determined. The standard deviation of the data for each treatment is therefore given.



TABLE I

EFFECT OF STARVATION AND EXERCISE ON THE CARBOHYDRATE RESERVES OF RATS  
(Averages for five animals per treatment)

Treatment of animals	Liver weight, gm.	Liver glycogen, mgm./gm.	Muscle pH*	Muscle lactic acid,* mgm./gm.
<b>Trial I</b>				
Untrained, ad lib. feeding	—	61.1	5.99	5.9
Trained, ad lib. feeding, no exercise	—	92.8	5.97	6.4
Trained, ad lib. feeding, 1 hr. exercise	—	41.2	6.15	5.4
Trained, starved 24 hr., 1 hr. exercise	—	0.3	6.44	4.6
<b>Trial II (all animals trained)</b>				
Ad lib. feeding, no exercise	5.76	41.5 ± 5.1	6.16 ± .02	5.12
Ad lib. feeding, 1½ hr. exercise	4.89	20.9 ± 7.5	6.59 ± .11	4.13
Ad lib. feeding, 3 hr. exercise	5.12	1.30 ± 0.8	6.70 ± .11	3.92
Starved 24 hr., no exercise	3.22	1.32 ± 0.4	6.49 ± .04	4.38
Starved 24 hr., 1½ hr. exercise	4.17	0.30 ± 0.05	6.87 ± .06	2.70
<b>Necessary differences for significance</b>				
Trial I, 5% level	—	11.8	Not significant	0.7
Trial I, 1% level	—	16.2	Not significant	1.0
Trial II, 5% level	0.91	**	**	0.95
Trial II, 1% level	1.24	**	**	1.29

\*24 Hr. after slaughter.

\*\*See text.

The data from Trial I indicate that the training received by the animals did not significantly alter the level of muscle carbohydrate, as evidenced by pH and lactic acid content 24 hr. after slaughter, but that a highly significant increase in liver glycogen did occur. However, this conditioning of the animal was not sufficient to allow it to continue the exercise for an hour without a significant reduction in liver glycogen and 24-hr. muscle lactic acid. Starvation combined with exercise increased the loss of carbohydrate reserves.

The data from Trial II show the expected progressive loss of reserve carbohydrate material with increasing amounts of exercise, although the difference between the 1.5- and 3-hr. periods was significant only in regard to liver glycogen. The 24 hr. starvation period depleted the liver glycogen to the same extent as did the 3 hr. exercise period and caused the most severe loss of liver weight of any of the treatments. However, the depletion of muscle reserves appears to have been slightly less severe than that caused by even a 1.5 hr. exercise period. Combined starvation and exercise caused the most severe loss of both liver and muscle reserves, the average glycogen and lactic acid values being significantly lower than those for any other treatment, and the pH value being the highest recorded though not significantly higher than that found for animals that had been exercised for three hours. Rather surprisingly, the liver weight of the starved animals increased during exercise; this may be related to the accumulation of lactic acid and other metabolites by this organ.

From these results it can be concluded that prolonged moderate exercise utilizes a considerable proportion of the carbohydrate reserves in both muscle

and liver. A 24 hr. starvation period, on the other hand, depletes the liver glycogen but necessitates only partial utilization of the muscle carbohydrate. The large standard deviation of the liver glycogen values after 1.5 hr. exercise (the range in liver glycogen was from 0.8 to 44.6 mgm. per gm.) indicates that the animals varied grossly in their ability to meet imposed exercise without undue depletion of reserves.

#### *Recovery of Carbohydrates in Rats*

To determine whether these animals were capable of replacing their carbohydrate reserves without ingestion of food, i.e. from the fat reserves of the body, and to obtain an estimate of the time required for replacement of reserves when food was supplied, 35 male rats were given the usual training, and then, with the exception of the control group, were starved for 24 hr. and exercised for one hour. One group of five rats was slaughtered immediately after the exercise, and other groups of five were allowed to recover for 6, 16, and 24 hr. without food, and for 6 and 12 hr. with free access to a high sugar synthetic diet.

The data obtained are presented in Table II. In the absence of food little redeposition of either muscle or liver glycogen occurred. A significant decrease in 24 hr. postslaughter pH, and an increase in lactic acid content of the muscle resulted from the first six hours of recovery period, and there was a significant increase in liver glycogen after 24 hr. recovery. However, there was no evidence of a progressive redeposition of reserve carbohydrate throughout the recovery period, and the maximum levels reached were far below those of the control animals.

When food was supplied, recovery was rapid and complete. Even within six hours, average values for liver weight, liver glycogen, muscle lactic acid, and muscle pH all differed significantly from those of the animals killed immediately after exercise, and the difference tended to increase during the subsequent

TABLE II  
RATE OF RECOVERY OF CARBOHYDRATE RESERVES IN RATS FOLLOWING  
STARVATION AND EXERCISE  
(Averages for five animals per treatment)

Treatment	Liver weight, gm.	Muscle pH*	Muscle lactic acid,* mgm./gm.	Liver glycogen, mgm./gm.
Controls, fed and rested	5.50 ± .36	6.21 ± .04	5.09 ± .30	33.76 ± 3.9
No recovery period	3.07 ± .36	6.77 ± .04	3.10 ± .30	0.36 ± 0.11
6 Hr. recovery, without food	3.64 ± .36	6.58 ± .04	4.12 ± .30	1.16 ± 0.48
16 Hr. recovery, without food**	3.66 ± .40	6.57 ± .05	3.61 ± .33	0.82 ± 0.27
24 Hr. recovery, without food**	3.36 ± .40	6.51 ± .05	3.99 ± .33	3.56 ± 0.87
6 Hr. recovery, with food	4.77 ± .36	5.91 ± .04	5.75 ± .30	72.48 ± 3.9
12 Hr. recovery, with food	8.34 ± .36	5.84 ± .04	5.69 ± .30	121.29 ± 3.9

\*24 Hr. after slaughter.

\*\*One animal lost from this lot.



six hour period. Deposition of liver glycogen was so pronounced that the glycogen content and liver weight significantly exceeded those of the control animals within 6 and 12 hr. respectively. Even the muscle carbohydrate reserves tended to exceed the level found in the control group although the differences did not achieve statistical significance.

#### *Recovery of Carbohydrate Reserve in Hogs*

Sixteen pigs of one uniform lot were numbered and divided at random into four treatments. All hogs were held overnight; one lot was left with water only, the others were fed 2 lb. of a 1:1 mixture of sugar and chop either 20, 8, or 4 hr. before slaughter. Blood samples were caught at the "stick", and psoas muscles were removed before the carcasses were cooled. Unfortunately three of the tattooed numbers were indistinct, and the carcasses could not be identified for removal of the psoas muscles.

Table III presents the average results obtained. The number of animals was not sufficient to give results of statistical significance, but the data suggest that more carbohydrate was present in the muscles eight hours after feeding than at longer or shorter times. The minimum muscle pH of 5.3 (3) was not attained by any of the animals in this test.

TABLE III  
EFFECT OF TIME OF FEEDING ON THE CONDITION OF HOGS AT SLAUGHTER  
(Averages for four animals per treatment)

Treatment of hogs	Blood sugar, mgm./100 ml.	Blood lactic acid, mgm./100 ml.	Muscle lactic acid,* mgm./gm.	Muscle pH*
Not fed	37.6	51.7	9.0	5.77
Fed 20 hr. before slaughter	45.2	46.5	8.7	5.69
Fed 8 hr. before slaughter	45.1	31.9	9.9**	5.58**
Fed 4 hr. before slaughter	42.2	55.1	8.3***	5.77***

\*24 Hr. after slaughter.

\*\*Two animals only.

\*\*\*Three animals only.

#### *Effect of Type of Feed on Hogs*

The efficiency of oat chop alone, and of chop mixed with an equal weight of sugar or molasses, was tested with three lots of 20 hogs each. All feeds were given at a rate of 2 lb. per hog 20 hr. before slaughter, but the chop-molasses mixture was not palatable until diluted with water. A considerable amount of this mixture was wasted by being spilled from the trough.

Table IV presents the average muscle pH and lactic acid content for these animals. The hogs fed chop and sugar yielded psoas muscles of lower final pH and higher lactic acid content than did those of the other two treatments. Those fed chop and molasses appeared to have deposited slightly less muscle

carbohydrate than those fed chop alone, but the difference, which may have been due to the unpalatable nature of the chop-molasses mixture, was not statistically significant.

TABLE IV  
EFFICIENCY OF VARIOUS FEEDS IN PROMOTING CARBOHYDRATE DEPOSITION  
IN HOG PSOAS MUSCLE  
(24 Hr. postslaughter determinations; averages for 20 animals per treatment)

Treatment of hogs	Muscle pH*	Muscle lactic acid, mgm./gm.
Fed chop	5.86	7.3
Fed chop plus sugar	5.66	7.7
Fed chop plus molasses	5.94	6.5

\*Necessary difference for significance, 5% level—0.16; 1% level—0.21.

### Discussion

The data presented in this paper show that moderate exercise alone depleted the muscle reserves of rats quite seriously, but that a 24 hr. starvation period plus moderate exercise was considerably more drastic. In current Canadian marketing practice, hogs are frequently received at the packing plant in a fatigued condition, are held overnight without food, and are subjected to additional exercise when driven from barns to shackling pens. Assuming that the results obtained with rats can be applied to hogs, it appears that this method of handling results in a minimum of reserve carbohydrate in the muscles at the time of slaughter. As previously shown (7), export (Wiltshire) bacon produced from such hogs is of lowered quality.

The data obtained with rats also indicate that redeposition of muscle glycogen did not occur if starvation was continued, but was completed within six hours when the animals had access to a high sugar food. The experiment with hogs was not conclusive, but suggests that eight hours was required with the larger animals. These results indicate that reserves depleted during the haul to the plant could readily be replaced by providing hogs with a chop-sugar mixture when they are received at the plant and holding them for at least six hours before slaughter. Provided the subsequent exercise imposed on the animals was not too severe, a considerable improvement in export bacon quality could probably be effected with a minimum disruption of plant schedules by this treatment. The economic aspects of such a practice have not been studied.

### Acknowledgments

The authors wish to express their sincere thanks to the statistical section under Dr. J. W. Hopkins for the analysis of the data, and to Mr. A. Lauzon for managing the rat colonies and for assistance with the analyses.

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## A PRECISION RADIO TIME SIGNAL SYSTEM<sup>1</sup>

BY D. W. R. MCKINLEY AND B. E. BOURNE

### Abstract

Precision seconds pulses are produced from a 100 kc. quartz crystal frequency standard, coded, and radiated from a 220 Mc. transmitter having line-of-sight coverage. The average jitter, or error in the interval between two seconds pulses, is  $10^{-2}$  sec. at the source, or  $10^{-6}$  sec. as observed at distant stations; this is several orders better than attainable with either the official Canadian or U.S.A. high-frequency time signal transmissions. The system has been used for continuous automatic time recording by a network of stations in a meteor observing program.

### Introduction

For several years a combined program of meteor observing has been in progress in the Ottawa area. The visual and photographic observations have been directed by the Dominion Observatory, and the radar, radio, and photo-electric methods have been the responsibility of the National Research Council, Ottawa. Accurate timing is demanded in all aspects of the program, of course, but the electronic techniques are particularly stringent in their requirements (3, 5, 6, 7). The range-time and amplitude-time photographic records of meteor echoes, obtained at four stations within a 40-mile radius about Ottawa, must be correlated in time to an accuracy of  $10^{-3}$  sec. or better. In the early days of the meteor work the Dominion Observatory official time signals (10) radiated from CHU on 3330 kc., 7335 kc., or 14,670 kc., were received at each of the observing stations and applied to the photographic records. The accuracy of these signals was of the order of one part in  $10^7$  or better over relatively long periods of time, but the timing error, or jitter between consecutive seconds was frequently as much as 0.02 sec., owing partly to the former mechanical keying arrangement at CHU (the present electronic keying method is more satisfactory) and partly to fading and poor signal-to-noise ratios at certain times of the day. The CHU seconds signals each consist of a burst of 1000-cycle tone, which is another limitation on short interval timing precision. The application of CHU signals to the photographic records has therefore been discontinued except as a stand-by service. However, the CHU transmissions are used to set and rate the N.R.C. quartz crystal clocks, and during meteor observing periods the signals are made available to the visual observers by means of loudspeakers.

The official Canadian primary standard of frequency is maintained at the National Research Council, Ottawa, and consists of five temperature-controlled 100 kc. quartz crystals. Four of these were supplied by General Radio, type C-21-HLD and type 1105-A, and one was manufactured by Western Electric,

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type D-173730. The rates of these quartz clocks are determined from star transit observations made at the Dominion Observatory, by means of the Observatory time signals transmitted to the N.R.C. laboratories over a land line. The long-term rates of the crystals can be predicted to one part in  $10^7$  over several months and the short-term stabilities are of the order of one part in  $10^8$ . The General Radio crystals are normally allowed to run without correction, but the Western Electric crystal is adjusted to maintain the crystal frequency at 100 kc. to better than one part in  $10^7$  and is used for the local standard frequency services. Daily checks with the U.S. Bureau of Standards transmissions from WWV on 10 Mc. rarely show discrepancies between the Canadian and U.S.A. standards in excess of a few parts in  $10^8$ .

### The N.R.C. Precision Time Signal System

To provide radio time signals of the desired precision at places within nominal line-of-sight of Ottawa it was first necessary to produce seconds pulses of short duration with intersecond jitters not more than  $10^{-6}$  sec., and then to radiate these pulses on a carrier frequency high enough to avoid ionospheric reflections. The block diagram, Fig. 1, outlines the time signal system that was designed to meet these requirements. The 100 kc. output frequency from the Western Electric crystal is divided in several stages to 1 kc. and this frequency is supplied to the 1 kc. General Radio Clock Type 1103-A. By electromechanical gating methods described in more detail in a previous paper (4) precision pulses are produced at the rate of 1 per sec. or 10 per sec. as desired; the relative jitter between pulses being of the order of  $0.1 \mu\text{sec.}$

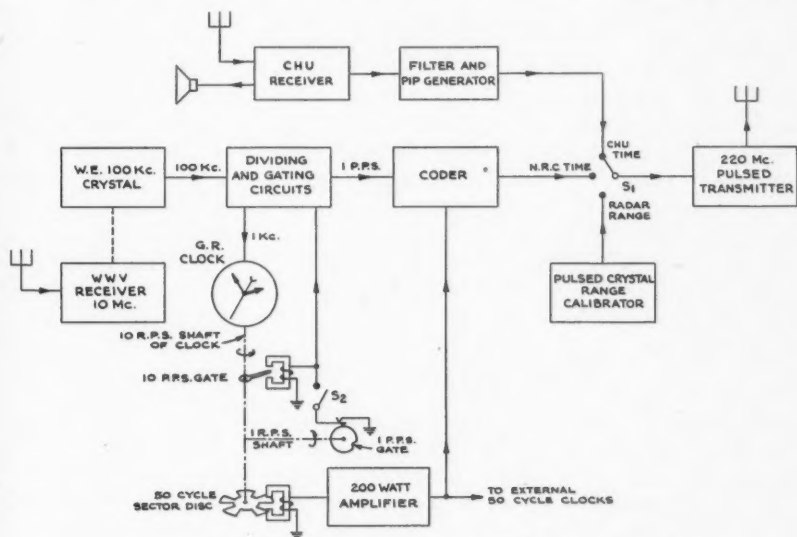


FIG. 1. Block diagram of the precision radio time signal system.

A five-sector disk on the 10 r.p.s. shaft of the 1 kc. clock generates a 50-cycle frequency which is subject to slight mechanical jitters but is entirely satisfactory for operating clocks and motors. The standard is chosen to be 50 cycles rather than 60 cycles to avoid difficulties that sometimes arise from nearly synchronous hum from the line frequency. A 200-w. amplifier provides adequate power at 110 v. to operate a number of clocks and small motors. The coder circuits perform two functions, first, they delete the 29th and the 58th and 59th seconds markers of every minute to permit the seconds of a given minute to be identified, and second, they produce a double pulse at the end of the  $n$ th second of the minute following the  $n$ th minute in the hour, so that the minutes may be identified.

With the switch  $S_1$  (Fig. 1) in the position *N.R.C. Time* the locally generated seconds pulses are sent to a transmitter which operates on a nominal carrier frequency of 220 Mc. and produces pulses each with a rise time of  $0.5 \mu\text{sec.}$  and a duration of  $15 \mu\text{sec.}$  The peak power is 5 Kw., radiated from an antenna on top of a 200-ft. tower at Ottawa. This transmitter was originally one of a chain of ground transponder beacons extending from Montreal, Que., to Windsor, Ont., and employed in operational trials of the distance measuring system developed in 1945-47 by the N.R.C. for air navigation. If the N.R.C. time signal system should fail at any stage prior to the 220 Mc. transmitter,  $S_1$  can be switched to *CHU Time*. The CHU receiver has tuned filters and pulsing circuits which produce short pulses from the 1000-cycle Observatory time signals. By re-radiating the modified CHU pulses on 220 Mc., uniformity of recording is ensured at all observing stations, although with reduced timing precision. If the 220 Mc. transmitter should fail, each station has a standard CHU receiver for independent emergency operation.

With the switch  $S_1$  at *Radar Range* the 220 Mc. transmitter radiates a series of pulses which enables the remote stations to calibrate their local range sweep circuits; this is usually done once or twice during an observing period. The pulsed crystal oscillator (2) produces a series of 15 or 20 pulses each accurately spaced  $133.4 \mu\text{sec.}$  (i.e., 20 km. range pips), whenever triggered by an external source, usually at a rate of 120 per sec. At the distant station the range sweep is started by the first pulse of the series and the standard range pips may be compared with the locally generated range pips to determine any corrections necessary to the latter. This pulsed crystal oscillator is based on a design by Brown (9) and is similar to circuits developed in England by Mynall (8).

### Some Features of the System

Most of the circuit techniques used in the N.R.C. time signals system are well known to the art and there would be little point in describing them at length, or in appending complete circuit diagrams. A somewhat more detailed review of the various functions outlined in the preceding section should suffice with emphasis on a few novel features which may be of interest.



The sinusoidal 100 kc. output from the Western Electric crystal is squared and differentiated to trigger a 20 kc. blocking oscillator, which in turn triggers a blocking oscillator at 5 kc., followed by another at 1 kc. Double triode 2C51 tubes are used, and in each case one half of the tube is the blocking oscillator and the other half is a cathode follower to provide a low impedance driving source of very short rise time for the next stage. Three stages instead of the usual two are used to reach 1 kc. from 100 kc. because of the greater ease of maintaining the correct division ratios. The blocking oscillator pulse transformers are designed to yield pulses about 5  $\mu$ sec. wide and with a very steep rise. The observed jitter of the precision pulses at the 1 kc. level is less than  $10^{-7}$  sec. The driving amplifier for the 1000-cycle General Radio clock is supplied with a sinusoidal wave form, obtained by integrating and filtering the 1 kc. pulses. Rather than divide the frequency further by means of purely electronic circuits with the possibility of introducing undesirable jitter, electromechanical gating methods (4) are used. A needle mounted on the 10 r.p.s. shaft of the General Radio clock produces an impulse voltage in a permanent-magnet pickup coil, which is then squared to form a gate pulse, approximately 100  $\mu$ sec. wide. By changing the position of the pickup coil the coarse gate pulse may be adjusted to straddle a precision pulse; in this manner 1 in 100 of the original 1000 pulses per second is selected without any deterioration of the pulse stability, and independently of jitter in the gate pulse. A cam switch rotating at 1 r.p.s. (the "microdial contactor" of the General Radio clock) may be connected across the output of the 10 pulses per second pickup circuit, and so phased that only 1 in 1000 of the 1000-cycle pulses is allowed to pass. The jitter in these selected pulses is, of course, the same as in the original 1000-cycle pulses, hence the intersecond jitter, or error in the interval between two seconds pulses is of the order of one part in 10 million. By holding open the one-second gating switch, either with a manual switch,  $S_2$ , or with a clock-driven cam, 10 pulses per second can be obtained. This is done automatically for a few seconds on the first minute of every hour as an auxiliary identification, in case the local 60-cycle clocks that print the hour and minute on the remote film records should become misaligned.

In the coder unit there is a cam switch rotating at 1 r.p.m. which is phased to remove the 29th and the 58th and 59th seconds markers of each minute. The seconds in a given minute can then conveniently be identified by counting from either of these breaks. Another cam switch, rotating at 1 revolution in 61 sec. and synchronized with the first cam switch, is used as a mechanical gate to allow every 61st pulse to trip a delay multivibrator. The multivibrator creates another pulse about 5 msec. after the selected pulse. Thus, for example, a double pulse is sent at the end of the fifth second after the fifth minute (the time at that instant being written 05<sup>m</sup> 05<sup>s</sup>), at the end of the sixth second of the sixth minute, and so on. When the 60th minute is reached an electromagnetic clutch operates to retard the mechanism for one second, otherwise the double pulse identifications would advance by one second during the second

hour. At the distant radar observing stations the normal seconds pulses are passed through gating circuits which produce two rows of spots on the cathode ray tube sweeps at 30 km. and 230 km. radar range. However, when a double pulse is received the whole trace is brightened momentarily. This is illustrated in the sample radar record, Fig. 2, which shows the bright trace marker at  $05^m 05^s$ , and a meteor echo beginning at  $21^h 05^m 04^s.5$  E.S.T. The range of the echo is 110 km. On the Doppler continuous-wave record, Fig. 2, the seconds pulses are applied directly to the sweep. The Doppler sweep has been triggered four times per sec. from a local tuning-fork oscillator which is not as stable as the primary crystal, hence the seconds pulses appear to drift slowly along the sweeps.

In the range-time recording of radar echoes from meteors the individual range sweeps are repeated at intervals of  $1/20$  sec., therefore the time resolution of the radar records is of the order of  $10^{-2}$  sec. The time resolution of the amplitude-time Doppler record shown in Fig. 2 is about  $10^{-3}$  sec. An improved Doppler recording system with a resolution of about  $5 \times 10^{-4}$  sec. is sometimes employed. To meet all requirements the time signals should have intersecond jitters of not more than  $10^{-4}$  sec. While the intrinsic precision of the seconds pulses as they leave the coding mechanism at Ottawa is about  $10^{-7}$  sec., small variable delays in the line to the 220 Mc. transmitter, in the transmitter itself, and in the receiving equipment increase the average intersecond jitter to about a microsecond, as observed over long periods of time. This is considerably better than demanded by present needs. To utilize the full potentialities of the system, corrections should be made for all measurable fixed delays, including the time of flight of the pulses between stations.

The N.R.C. time signal receivers are conventional superheterodynes having two stages of r.f. amplification at 220 Mc. using grounded-grid triodes, and an i.f. frequency of 30 Mc. with a nominal band width of 6 to 8 Mc. One feature of interest is the discriminator circuit used in the second detector to reject both adjacent-channel pulse signals and continuous-spectrum noise interference from ignition sources or atmospherics. This circuit was first invented by H. A. Ferris, at the National Research Council in 1944, with further development being done by Federal Telecommunication Laboratories, Nutley, N.J., and by Telecommunications Research Establishment, Great Malvern, England. It is shown in Fig. 3 in modified form. The transformer coupling is adjusted to produce a double hump in the voltage-frequency curve measured at *A* on the primary, and a single hump in the curve measured at *B* on the secondary. The primary curve is subtracted from the secondary curve by means of the diodes connected as indicated to yield the video output response curve shown at *C*. For frequencies falling within a band  $\pm 1.5$  Mc. about the center frequency, the output is positive, but for signals falling outside these limits the output is negative. Only positive signals are utilized in subsequent circuits. The measured discrimination against a pulse transmitter operating 2.5 Mc. either side of the desired carrier frequency is more than 100 db. In the case of ignition noise with a broad spectrum of frequencies it is necessary to

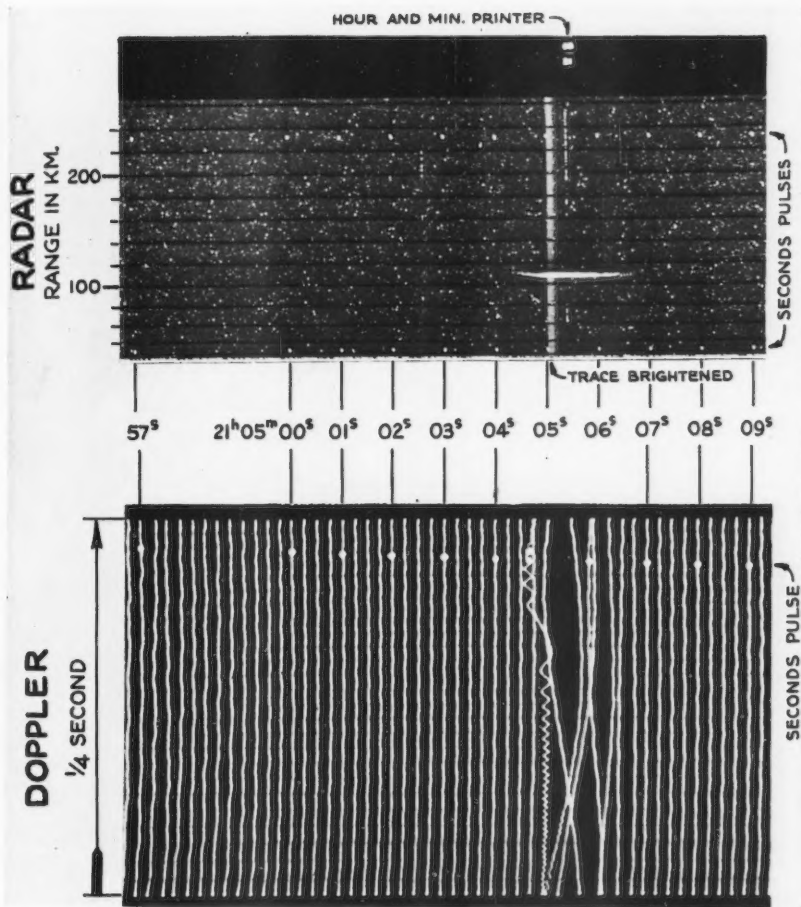


FIG. 2. Simultaneous radar range-time and Doppler C.W. amplitude-time records, showing applications of precision time signals. The meteor echo appears as intensity-modulation of the radar sweep, and as amplitude-modulation applied transversely to the Doppler sweep.

e  
c  
f  
a  
v  
l

ensure that the i.f. band width is wide enough to admit more energy on frequencies outside the 1.5 Mc. points of the curve *C* than within them, thus making the net pulse output negative. The interfering pulse or noise signal punches a "negative hole" in the video output, and if this hole should happen to coincide with a desired signal the latter may be cancelled. For pulse reception, where both the desired and undesired pulses are very short in comparison with the

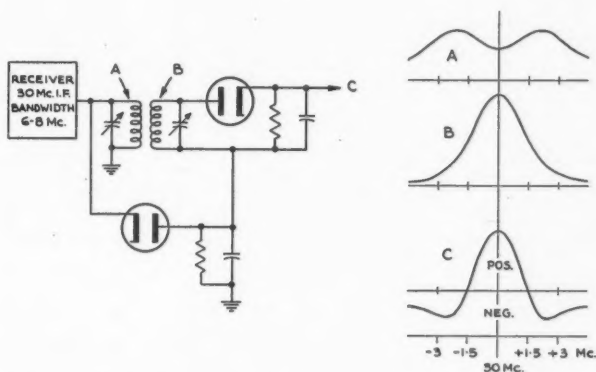


FIG. 3. Second detector discriminator used in the time signal receivers to suppress adjacent-channel pulse signals and impulse noise.

intervals between pulses and the probability of pulse cancellation is small, this circuit is highly efficient, but it will not be effective against continuous-wave interference. This discriminator has contributed to the success of the 100 Mc. distance measuring equipment developed by the Federal Telecommunication Laboratories and is an integral part of air navigation equipment approved for civil aviation by the U.S. Civil Aeronautics Administration (1)

The N.R.C. time signal system was put into service in the spring of 1949. At present it functions only when needed by the meteor observing project though it is planned to operate it continuously if warranted by the demand of other local users. Neither CHU nor WV time signal transmissions are suited to continuous automatic recording techniques, partly because their modulation methods are designed to accommodate a wide clientele and have not the short-interval precision required in our work, and partly because of the disturbing effects of multipath transmissions, interfering signals, and local noise. Use of a high carrier frequency in the N.R.C. system avoids these difficulties but at the same time limits the coverage to approximately line-of-sight distances, similar to FM or TV broadcast ranges. The long-term accuracy of the N.R.C. signals is about one part in 10, or somewhat less than that of either CHU or WWV, as might be expected since these latter transmissions constitute the fundamental primary time services of Canada and U.S.A. respectively. However, the short-term, or intersecond precision of the

N.R.C. time signals is much higher than the usable short-interval precision of the official sources. While some of the particular features of the N.R.C. system have been adapted to local requirements the basic design may be of general interest wherever a need exists for precise short-interval timing suited to automatic recording.

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## AN INVESTIGATION OF THE CORROSION OF DOMESTIC HOT WATER TANKS<sup>1</sup>

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### Abstract

A method for the examination of corrosion in domestic hot water tanks is described. Results based on physical and metallographic examination of tanks taken from 15 localities in Ontario are given. Evidence is presented to show that the polarity of the zinc-iron couple reverses under certain service conditions. Discussion of the causes of failure and possible methods of prevention are included.

### Introduction

The records of Central Mortgage and Housing Corporation over the past few years indicate that a considerable number of domestic hot water tanks have failed by corrosion after a short service life in certain localities. This represents an economic loss because of replacement costs. An investigation of this problem was undertaken by the National Research Council at the request of Central Mortgage and Housing Corporation. Although the problem exists in varying degrees throughout Canada, the initial study of this problem was confined to Ontario.

A summary of records of tank performance compiled for a period of six months appears in Table I.

The general problem of the corrosion of galvanized hot water tanks has been studied extensively by Hoover (6) and Bialosky (1). Similarly, the corrosion of zinc and zinc coatings on steel in aqueous media has been studied by several investigators (3, 4, 5, 10). A number of papers (2, 7, 8, 13) have been published reporting on the mechanism of corrosion of zinc coatings in hot water under laboratory conditions. Evidence has been presented in these reports to indicate that a reversal of polarity of the zinc versus steel couple sometimes occurs in service.

This paper reports on tanks which failed in service and includes:

1. Percentage failures;
2. Physical examination;
3. Metallographic examination.

In the investigation described here photomicrographs were made of the zinc coatings on steel. These were taken from tanks which had failed in service under various conditions in order to observe the mechanism of failure and to

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detect, if possible, evidence of the reversal of polarity. The methods used by Rowland and Romig (12) for metallographic examination of zinc coatings were adapted for this investigation.

TABLE I  
RECORDS OF TANK SERVICE FOR PERIOD NOVEMBER, 1949 TO APRIL, 1950

Locality	Type of tank	Age of project, yr.	Total no. of houses	Total no. of tank failures*	Av. service life of failed tanks, yr.	Tanks examined
Brantford	Standard	3½	647	30	3	1
	Wartime	6	50	5	6	
Hamilton	Standard	6	1531	7	3	6
	Wartime	6	731	20	6	7
Collingwood	Standard	6	136	2		
	Wartime	6 to 7	120	9	5 to 6	
North Bay	Standard	3	106	14	3	1
	Wartime	1 to 2	108	3		1
Kingston	Standard	7 to 8	300	10	7 to 8	
	Wartime	1½	219	4	1½	1
Renfrew	Standard	6½	22	1	2½	
	Wartime	3	127	23	2	17
Lindsay	Standard	4	50	38	3 to 4	
	Wartime	6	131	18	6 to 7	3
Malton	Standard	3	93	0		
	Wartime	6	107	17	6	2
St. Catharines	Standard	9	225	16	8	1
	Wartime	6 to 7	150	18	7	
Port Hope	Standard	5	72	8		8
	Wartime		70			
Belleville	Standard	2	103	44	1 to 3¼	3
	Wartime	3	25	8	3¼	2
Campbellford	Standard	3½	100	1	2½	1
	Wartime					
Smiths Falls	Standard					1
Ottawa	Standard	2				1

### Experimental

The laboratory investigation consisted of physical and metallographic examination. A routine procedure was developed for cutting open the tanks to obtain suitable samples. The method of cutting is illustrated in Fig. 1 and the areas from which the samples were taken are illustrated in Fig. 2. The samples for the metallographic examination were taken from the areas which were examined physically in order to provide a basis for correlation.

#### A. Physical Examination

The inside surfaces of the tanks were photographed to provide a record of their appearance. Representative samples of these are illustrated in Figs. 5, 6, 7, 8, and 9. General observations were also recorded.

Physical measurements were made on the areas designated in Fig. 2 and consisted of the following:

1. Wall thickness;
2. Total pits counted and recorded as pits per 10 sq. in.;
3. Depth of all pits (recorded as average depth).

\* These tank failures are for the designated six month period. The rate of failure before this time is not known and for this reason the apparent service life of the wartime tanks is probably not representative.

The zinc thickness was measured on the outside of the tank. Five measurements were made, located in the plane of the vertical axis spaced about one foot apart. The measurements were made with a General Electric Thickness Gauge, Type B.

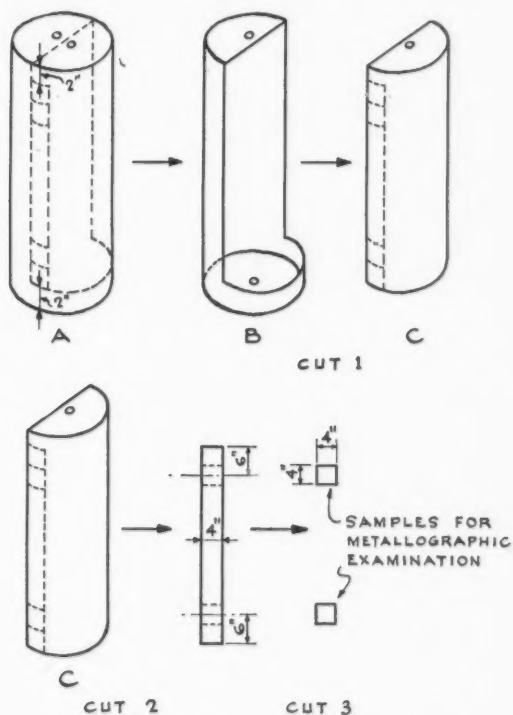


FIG. 1. Method of cutting a tank for examination.

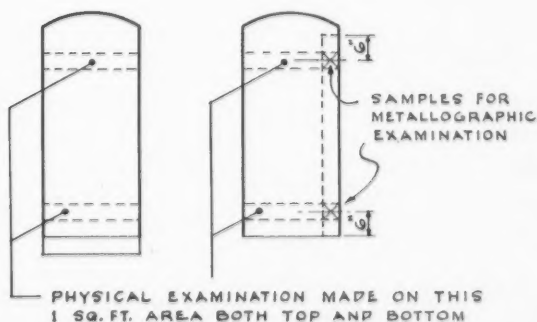


FIG. 2. Areas marked for examination.

### *B. Metallographic Examination*

#### *Procedure*

Specimens were cut from the samples indicated above, dipped in bakelite lacquer, drained, baked dry at 275° F., and mounted in bakelite. The lacquer coat improved the edge preservation. The mounted specimens were then ground down to 4/0 emery paper in the normal fashion. Preliminary wet polishing was done on silk cloth using a special levigated alumina buffered to a pH of 7. The final polish was done on Kittens Ear broadcloth with the same abrasive. At no time were the specimens washed with water because this tended to stain and etch the zinc. Specimens were always carefully wiped off with cleansing tissue. The following etches were found satisfactory for all the specimens:

1. 0.15 gm. picric acid  
50 ml. water  
10 ml. ethanol
2. 0.075 gm. picric acid  
50 ml. water  
10 ml. ethanol.

The first was used for the corroded edge, and the second for the outside edge. The complete edge of each specimen was examined and photomicrographs were made of portions that were fairly representative. The photographs were made on metallographic plates using a Leitz Panphot microscope. All are at a magnification  $\times 250$ .

## **Results**

### *A. Analysis of Water*

Analysis of the tap water from the five localities included in this investigation are compiled in Table II.

### *B. Physical Examination*

#### *Wall Thickness*

Two general types of tanks were examined. These were classed as the "wartime" and the "standard". The wall thickness of the wartime tanks varied between 0.070 and 0.077 in. with an average of 0.075 in. The standard tanks had a wall thickness in the range of 0.080 to 0.092 in. with an average of 0.085 in.

#### *Zinc Coatings*

It was assumed that the zinc coating on the outside of the tanks was representative of the zinc coating on the inside. Visual observation suggested that this assumption was perhaps erroneous, and it appeared that the coating on the inside was not as good as that on the outside. It was noted that more dross inclusions were found in the inside coating.

The thickness of the zinc coatings as measured on the outside surfaces of the tanks varied over the range 2 to 6 mils. Data presented in Fig. 3 show the

TABLE II  
ANALYSES OF CIVIC WATER SUPPLIES

	Sample point				
	Plant tap		Lab. tap	Town tap	
	Locality and source of water				
	Belleville, Ont. Bay of Quinte	Hamilton, Ont. Lake Ontario	Lindsay, Ont. Scugog River	Ottawa, Ont. Ottawa River	Port Hope, Ont. Lake Ontario
pH	7.5	8.3	7.8	8.4**	8.3
Color	10	0	15	4**	0
Turbidity	4.6	1.1	algae	6.0	0.4
Spec. conductance*	217.1	302.8	223.2	61.16	298.6
Residue on evap.					
Dried at 105° C.		175.8	160.8	64.0	173.6
Ignited at 530° C.		150.6	109.6	36.6	155.2
Alk. as CaCO <sub>3</sub>					
(phenolphthalein)	0	2.0	0	0	5.6
Alk. as CaCO <sub>3</sub> (MeO)	83.4	100.0	104.0	31.2	98.0
Calcium (Ca)	39.3	39.8	39.8	6.7	40.3
Magnesium (Mg)	3.8	10.4	7.9	2.7	8.6
Sodium (Na)	2.0	8.6	3.0	4.2	8.7
Potassium (K)	1.2	1.6	1.0		1.1
Sulphate (SO <sub>4</sub> )	41.4	24.5	22.8	11.7	27.7
Chloride (Cl)	1.0	18.6	5.9	2.3	18.5
Nitrite (NO <sub>2</sub> )				0	
Nitrate (NO <sub>3</sub> )		1.8	2.2	.8	1.3
Bicarbonate (HCO <sub>3</sub> )	101.8	117.1	126.9	27.4**	105.9
Carbonate (CO <sub>3</sub> )		2.4	0	2.1**	6.7
Silica (SiO <sub>2</sub> ) grav.		2.6	1.4	8.0	3.2
col.	4.8	2.1	2.0	5.6	1.9
Hardness as (CaCO <sub>3</sub> )					
Noncarbonate	30.9	42.1	27.8	0	37.9
Total	114.3	142.1	131.8	27.9	135.9

\*Micromhos at 25° C.

\*\*Average of daily results for 1948 from filtration plant.

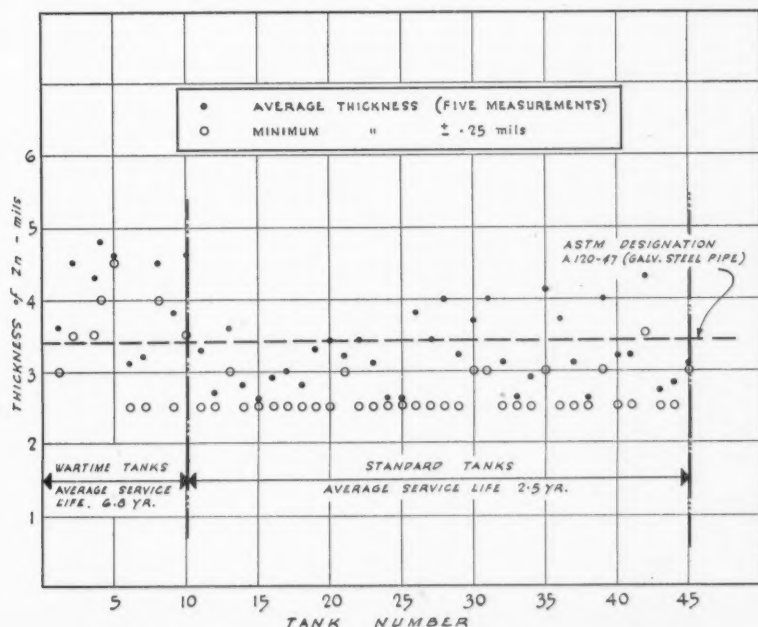


FIG. 3. Thickness of zinc coatings on individual sample tanks.

average and the minimum thickness of zinc coatings on the tanks examined. Deviation of the minimum thickness from the average on any one tank was found to be 0.5 to 1.5 mils. Similar variation in the thickness of the zinc coating could be found on an area of 1 sq. in. of some of the tanks.

### *Pits*

The size and number of pits per unit area were characteristic of the locality where the tanks were in service. Figs. 7 and 8 illustrate this point. Considering the area of 1 sq. ft. at the top of the tanks, the average number of pits per 10 sq. in. varied from 0.3 to 30. These data could not be correlated with service life. Similarly the average pit depth for the area in question varied from 0.025 to 0.060 in. at the time when several pits had produced holes in the wall of the tank. Pits on tanks from localities such as Hamilton, Lindsay, Port Hope, and Ottawa were covered with caplike nodules of corrosion products as shown in Figs. 5, 7, 8, and 9. In the case of the tanks from Belleville the pits exposed shiny metal (Fig. 6).

### *C. Metallographic Examination*

In all, 185 photomicrographs were made from samples of 46 tanks taken from 15 different localities. The majority of those examined were from Hamilton, Lindsay, Port Hope, and Belleville. Photomicrographs of tanks from these localities and one tank from Ottawa have been included. The nomenclature used in describing the layers of the coating is the same as that used by Daesen (4) and Rowland (11). These designations are indicated in Fig. 10.

The photomicrographs are arranged in groups of three, showing cross sections of (A) the outside zinc coating, (B) the inside corroded zinc coating at the top of the tank, and (C) the inside corroded zinc coating at the bottom of the tank.

## **Discussion**

The corrosion of domestic hot water tanks involves the destruction by electrochemical action of galvanized steel in the presence of water and is affected by the following variables:

1. Water composition;
2. Temperature;
3. Rate of flow of water or total volume of water;
4. Variation in the thickness of the zinc coating;
5. Porosity of zinc.

Assuming a perfect tank the initial corroding system consists of water in contact with the outer layer of pure zinc which is pore-free and continuous.

If the zinc corrodes evenly and without forming a protective layer, the life of the tank will be determined by the rate of the corrosion of the zinc, the rate of penetration of the steel by corrosion and/or pitting, and by the thickness of the zinc and the steel. Examples of this are the tanks from Lindsay, Ont., where the zinc corrodes evenly with time (Fig. 12). When the zinc no longer



covers the steel, owing either to the removal of zinc by corrosion or discontinuous initial application, the life of the tank becomes dependent upon the pitting rate of the steel in the water. Corrosion by pitting is an erratic and unpredictable process. The useful service life of a tank must be considered as that period before pitting begins.

Continuous zinc coating is the initial barrier against pitting. The final barrier which leads to long tank life is a scale deposited from the heated water on the tank surface. The scale may or may not contain corrosion products. If the deposited scale is not protective (or if no scale is deposited) the zinc will protect the iron if it is anodic to the iron, for a period depending upon the rate of corrosion of zinc in the hot water and the thickness of the zinc layer. The rate of corrosion of zinc in hot water is generally high.

Theoretically zinc, being the more electronegative metal, protects steel in aqueous environment by acting as a sacrificial anode. Therefore, small areas of exposed steel should be protected as long as they are surrounded by a layer of zinc. However, the results of the metallographic examination of corroded edges showed that this was not always the case (Figs. 10, 11, 13, and 14). Pitting of steel has been observed adjacent to areas where most of the zinc coating was still present, as shown in Fig. 11. Separation of the eta layer from the remaining zinc coating and the corrosion of the zeta layer in the presence of the eta layer was observed and is shown in Figs. 10, 13, and 14. This observation confirms the reversal of polarity between eta and zeta layers as well as between steel and the zinc coating. Results of laboratory investigations by a number of workers (7, 8), and (13) indicate that under certain conditions of temperature and composition of water, the polarity of the zinc-iron couple reverses. The above is evidence of this happening under service conditions.

The measured thickness of zinc on the tanks examined is shown in Fig. 3. It indicates the fact that most of the tanks which had a service life of less than three years had areas of zinc coating less than 3.4 mils which is the minimum thickness of zinc specified by A.S.T.M., Designation A 120-47, for zinc coatings on steel pipe. It may be noted that the groups of tanks which had a service life of over six years in most cases had a minimum thickness of zinc exceeding 3.4 mils.

The present method of tank manufacture does not allow application of a uniform coating of zinc to the inside surfaces. Streaky accumulations of zinc as well as large areas of dross were observed on the surfaces. This is the result of application of the zinc coating after the tank has been made. The flux and spelter must be introduced through small openings in the tank and because of this, complete fluxing of surfaces and uniform drainage of the spelter is not achieved.

Generally, with an evenly corroding system, the rate of attack will be increased by increasing the temperature. This was observed in tanks where temperature gradients existed owing to the method of heating. Fig. 4 illus-

trates the temperature distribution found in a tank full of hot water when three different types of heaters were used. In the tanks examined the distribution and depth of pits along the height of the tank were related to the temperature variation. When no temperature gradient existed as in the case

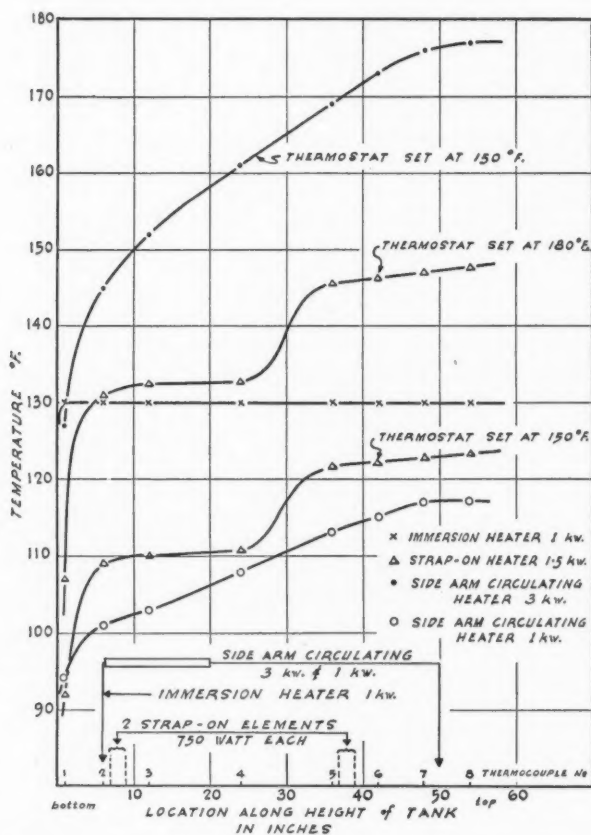


FIG. 4. Variation of the temperature of the water along the height of the tank heated by means of three types of electric heaters.

when an immersion heater was used, the number and depth of pits were nearly constant. Sample tank, Fig. 7, is an example of this case. When a side arm circulating heater was used the depth and number of pits increased with height of tank from the bottom. The depth of the pits at the top was twice the depth of the pits at the bottom in tanks heated in this manner, (Fig. 6). Several tanks were examined which were heated by means of a strap-on heater element

placed around the tank at a location about two ft. from the bottom. In these cases there was no evidence of pitting in the tank below the heater location whereas serious pitting of the tank occurred above the heater location, resulting in failure. From Fig. 4 it is evident that water would be heated only above the location of the strap-on element and there would be no tendency for the water below the heater to circulate and mix with the hot water.

It is interesting to note that there is a poor relationship between the temperature setting of the commercial thermostat and the temperature of the water.

A large number of recent installations of hot water systems consist of a galvanized tank connected with copper tubing. This is not good practice because dissimilar metals constitute an electrochemical cell and may accelerate the corrosion of one metal. In addition, it has been reported by Kenworthy (9) that traces of copper which may be dissolved in such a system would deposit on the zinc coating of the galvanized tank, resulting in local failure. The effect of the above factors is, however, difficult to evaluate in an investigation such as this. At least half of the tanks examined had been connected with copper tubing, the remainder with galvanized iron pipe. From the data available no conclusions can be drawn.

A survey of the performance of a large number of tanks in one locality revealed that tanks equipped with 3-kw. heaters (manually controlled) gave longer service than tanks equipped with 500-w. heaters (automatically controlled). Study of the method of operation of the two groups of units revealed one significant difference. The heaters of the first group were operated intermittently resulting in the storage of hot water for a relatively short period each day, the capacity of the heater being large enough to meet the demand after being on for two to three hours. The heaters of the second group being of low capacity were left on continuously resulting in the storage of hot water in the tanks for the greater part of each day. Thus it would appear that tanks using large heaters operated intermittently constitute the better system. The thermostat should be used only as a safety device.

Four tanks from Lindsay had magnesium anodes for cathodic protection. The average service life of these tanks was one year and seven months. Fig. 9 illustrates the condition of a typical anode after use and the appearance of the tank in which it was installed. The appearance of the inside of this tank was similar to that of the standard tank not equipped with a magnesium anode (Fig. 8). The deterioration of the anode appears to be due to local action between the magnesium and the steel core upon which it was cast. It is evident that this type of magnesium anode does not protect the tank and hence does not improve the service life of a galvanized tank in service at Lindsay.

An improved design of magnesium anode might be more effective than those used in Lindsay, especially if it was used in areas where the water has a high conductivity and the ability to deposit a protective scale.

### Corrosion Prevention

The methods of preventing or decreasing the corrosion of hot water storage tanks can be listed generally as follows:

1. Improved design of tanks and better manufacturing control, using existing materials;
2. Treatment of water;
3. Cathodic protection;
4. Use of other materials for tanks.

As was discussed above, a thick uniform coating of zinc is desirable even under the best conditions and therefore all possible effort should be made to achieve this. If necessary, the design of the tank should be changed to allow for close inspection during manufacture and this should result in a better quality product.

The characteristics of the water are basic when considering corrosion prevention. A great deal has been written regarding the various methods of treating water to make it less corrosive. These methods usually involve considerable cost when the entire supply of water is to be treated. Less than 25% of domestic water supply is heated and passes through the hot water system where, because of the higher temperatures involved, corrosion is the greatest problem. It is suggested therefore, that the use of corrosion inhibitors such as polyphosphates or silicates be considered to protect individual household hot water systems. This would involve the treatment with inhibitor of a relatively small quantity of water. A program to test the usefulness of these inhibitors in hot water tank systems is now being initiated.

### Acknowledgments

The authors wish to thank Central Mortgage and Housing Corporation for making available sample tanks and performance records, and especially Mr. I. E. Ashfield, Supervisor, Technical Department, for his interest in the project; Mr. C. S. Parsons, Director of Mines Branch, Department of Mines and Technical Surveys, for making available water analyses through the kind co-operation of Mr. J. F. J. Thomas, who contributed useful ideas; Mr. P. Beaubien of the Chemistry Division for producing the photomicrographs; and Dr. W. P. Dobson, Director, and members of the staff of the Research Division of the Hydro Electric Power Commission of Ontario, in particular Mr. D. Watt for his special interest in this problem.

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## EXPLANATION OF PLATES

## PLATE I

- FIG. 5. Sample of standard tank in service at Port Hope, Ont., for two years. Failed by pitting.
- FIG. 6. Sample of standard tank in service at Belleville, Ont., for two years. Failed by pitting. (Note cross inclusions and lack of corrosion products over pits.)
- FIG. 7. Sample of standard tank in service at Hamilton, Ont., for three and one-half years. Failed by pitting.
- FIG. 8. Sample of standard tank in service at Lindsay, Ont., for two and three-quarter years. Failed by pitting.
- FIG. 9. Sample of a tank and the magnesium anode (used to provide cathodic protection) in service at Lindsay, Ont., for two years. Failed by pitting.

## PLATE II

FIG. 10. Samples from Hamilton. ( $A_1$  and  $A_2$ ). Outside zinc coating—showing the zinc alloy layers and the steel base; 1, eta; 2, zeta; 3, delta<sub>1</sub>; 4, gamma; 5, steel. ( $B_1$  and  $B_2$ ). Inside top—showing the steel, the slightly attacked delta<sub>1</sub> layer, the blistered zeta layer, the complete replacement of the eta phase by corrosion products (c), and the scale (b) deposited by the water. ( $C_1$  and  $C_2$ ). Inside bottom—similar to ( $B_1$ ), except that the eta layer has been partially replaced by corrosion products and there is a thicker scale deposited from the water. The bakelite lacquer and the bakelite mount marked (a) are visible above the scale in  $C_1$ .

## NOTE:

1. The indication of polarity reversal between the zeta layer and the delta<sub>1</sub> layer, as evidenced by the failure of the zeta layer to completely protect the delta<sub>1</sub> layer.
2. That there is a heavy scale formed from the hard water which is not too protective.

## PLATE III

FIG. 11. Samples from Ottawa. (A). Outside zinc coating—showing the steel, the gamma, the delta<sub>1</sub>, the zeta, and the eta layers. (B). Inside top—showing the steel, the delta<sub>1</sub> layer, the pitted zeta layer, the complete replacement of eta by corrosion products, some scale, the lacquer, and the bakelite. (C). Inside bottom (unetched)—showing the pitted steel and the remainder of the zinc.

## NOTE:

1. The indication of polarity reversal between the zinc and the steel as evidenced by the failure of the zinc to protect the steel.
2. That the scale was nonprotective.

FIG. 12. Samples from Lindsay. ( $A_1$  and  $A_2$ ). Outside zinc coating—showing the steel, and the alloy layers (Fig. 10). ( $B_1$  and  $B_2$ ). Inside top—showing the steel, some gamma, the delta<sub>1</sub>, the slightly blistered zeta layer, the complete replacement of the eta layer by corrosion products, the bakelite lacquer and the bakelite mount. Note that there is some evidence of a scale deposited from the water on  $B_2$ . ( $C_1$  and  $C_2$ ). Inside bottom—similar to ( $B_1$ ) except that the zeta layer shows no blistering and some of the eta layer remains. There is some evidence of scale deposited from the water on  $C_2$ .

## NOTE:

1. That no reversal of polarity is indicated between the phases of the zinc coating.
2. That in spite of Lindsay's comparatively hard water there is no evidence of heavy scaling. The scale that does form is nonprotective.
3. That there would be a linear relationship between tank life and the thickness of the zinc coating (secondarily the thickness of the steel).

## PLATE IV

FIG. 13. Samples from Port Hope. ( $A_1$  and  $A_2$ ). Outside zinc coating—showing the steel, the gamma, delta<sub>1</sub>, zeta, and eta layers. ( $B_1$  and  $B_2$ ). Inside top—showing the steel, some gamma, the attacked delta<sub>1</sub> layer, the blistered zeta layer, the complete replacement of the eta layer by corrosion

products, and some evidence of scale deposited from the water. ( $C_1$  and  $C_2$ ). Inside bottom—showing the steel, the gamma, delta<sub>1</sub>, and zeta layers fairly intact, the partial replacement of the eta layer by corrosion products, and some evidence of a scale deposited from the water.

NOTE:

1. That there is an indication of a reversal of polarity between the zeta and delta<sub>1</sub> layers of the zinc coating.
2. That the scale deposited from the water is only slightly protective.

FIG. 14. Samples from Belleville. ( $A_1$  and  $A_2$ ). Outside zinc coating—showing the steel, the gamma, delta<sub>1</sub>, zeta, and eta layers. ( $B_1$  and  $B_2$ ). Inside top—showing the steel, some gamma, the attacked delta<sub>1</sub> layer, the blistered zeta layer, the complete replacement of the eta layer by corrosion products, and some evidence of scale deposited from the water. ( $C_1$  and  $C_2$ ). Inside bottom—showing the steel, the gamma, delta<sub>1</sub>, and zeta layers fairly intact, the partial replacement of the eta layer by corrosion products and some evidence of a scale deposited from the water.

NOTE:

1. That there is an indication of a reversal of polarity between the zeta and delta<sub>1</sub> layers of the zinc coating.
2. That the scale deposited from the water is only slightly protective.



PLATE I



FIGURE 5



FIGURE 8



FIGURE 6



FIGURE 9



FIGURE 7

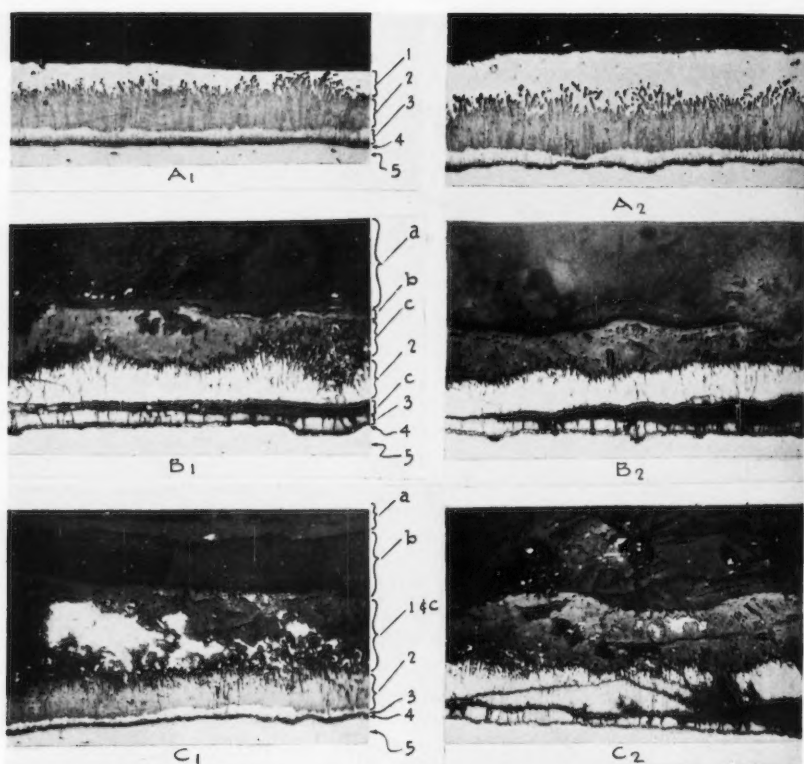


FIGURE 10 SAMPLES FROM HAMILTON

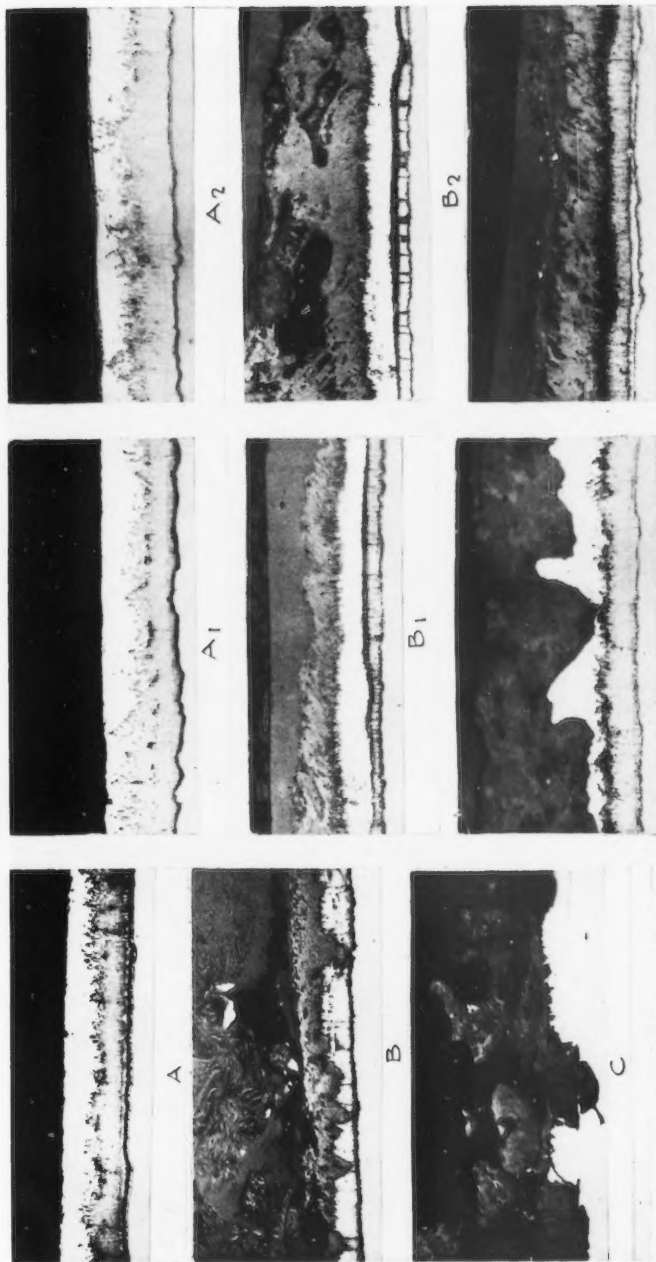


FIGURE II SAMPLES

FROM OTTAWA

FIGURE I2 SAMPLES FROM LINDSAY

C<sub>1</sub>

C<sub>2</sub>

B<sub>1</sub>

B<sub>2</sub>

A<sub>1</sub>

A<sub>2</sub>

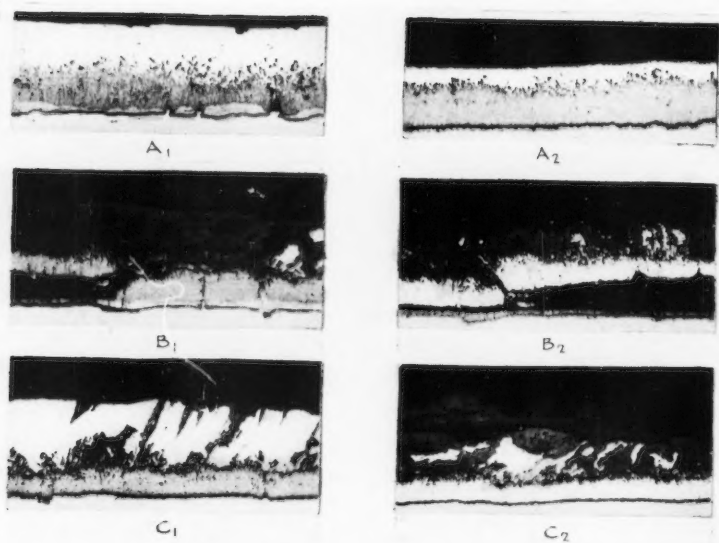


FIGURE 13 SAMPLES FROM PORT HOPE

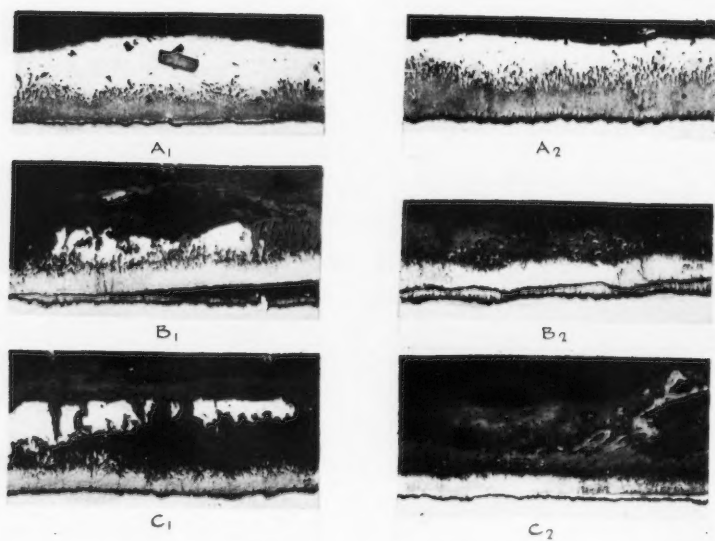


FIGURE 14 SAMPLES FROM BELLEVILLE

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NOTE

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**Photoelectric Vacuum Controller\***

One of the major problems in precise vacuum distillation is accurate control of the pressure. References to a number of devices designed for this purpose are given in papers by Huntress and Hershberg (1) and Todd (2). Principal objections to many of these devices are the intricate glassware required, the use of metal to mercury contacts which tend to become dirty, and the necessity of a separate pressure gauge for setting and checking the device.

In some work on vacuum distillation of fatty acid esters the authors have developed a controller which has proved extremely satisfactory over the range 1 to 20 mm. and has overcome the above-mentioned difficulties. The controller consists of a Dubrovin vacuum gauge,\*\* light source, photocell, and electronic relay. Interruption of the light beam by the float in the Dubrovin gauge provides the control mechanism.

The arrangement of the component parts is shown in Fig. 1. Light from A, a 6 v., 1 amp. exciter lamp, is directed on photocell B by means of a 1 mm. pinhole C in the light housing. The photocell, appropriately housed to eliminate stray light, is connected to the electronic relay as shown in Fig. 2.

When the photocell is energized by the light beam the electronic relay is closed. As the pressure in the system decreases, the float D in the Dubrovin gauge rises until it interrupts the light beam, de-energizing the photocell and causing the relay to open. The controller thus provides for discontinuous operation of the vacuum pump, or where continuous operation of the vacuum pump is desired, it may be used to operate a solenoid valve.

Since the Dubrovin gauge is a direct, continuous reading instrument, the control point is set by sliding the photoelectric assembly on the upright bar until the pinhole in the light housing is opposite the desired value on the gauge scale. Precision of control depends on the distance travelled by the float between the points where the photocell is energized and de-energized. In the unit constructed in this laboratory the total float travel was approximately 1.5 mm. giving pressure control to  $\pm 0.1$  mm. The float had a slight tendency to lag and it was found that this variation could be reduced to one half the above value by attaching a small vibrator to the gauge. The unit was installed on a commercial laboratory vacuum distillation apparatus in place of the mercury manometer type supplied. Temperature variation at the head of the column during the distillation of methyl esters of fatty acids was  $\pm 0.25^\circ\text{C}$ . at 10 mm. pressure.

\* Issued as N.R.C. No. 2510.

\*\* Type B, range 0-20 mm., magnification 9 to 1.  
Purchased from W. M. Welch Manufacturing Co.

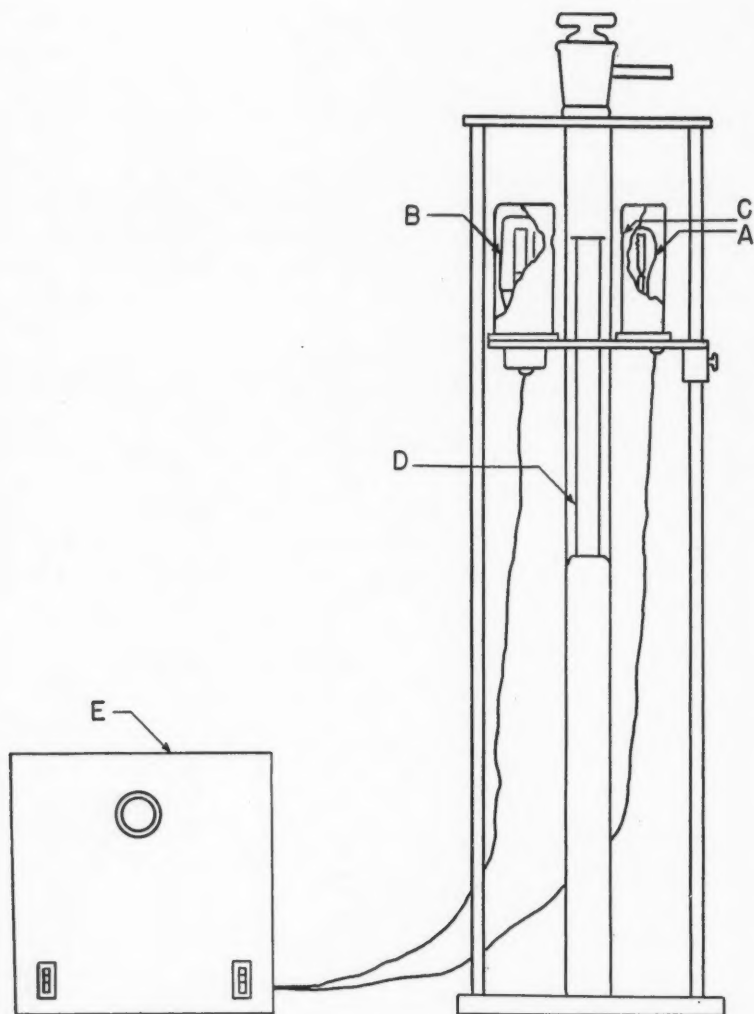


FIG. 1. Arrangement of component parts.  
A—light source  
B—photocell  
C—pinhole in housing  
D—float of Dubrovin gauge  
E—electronic relay



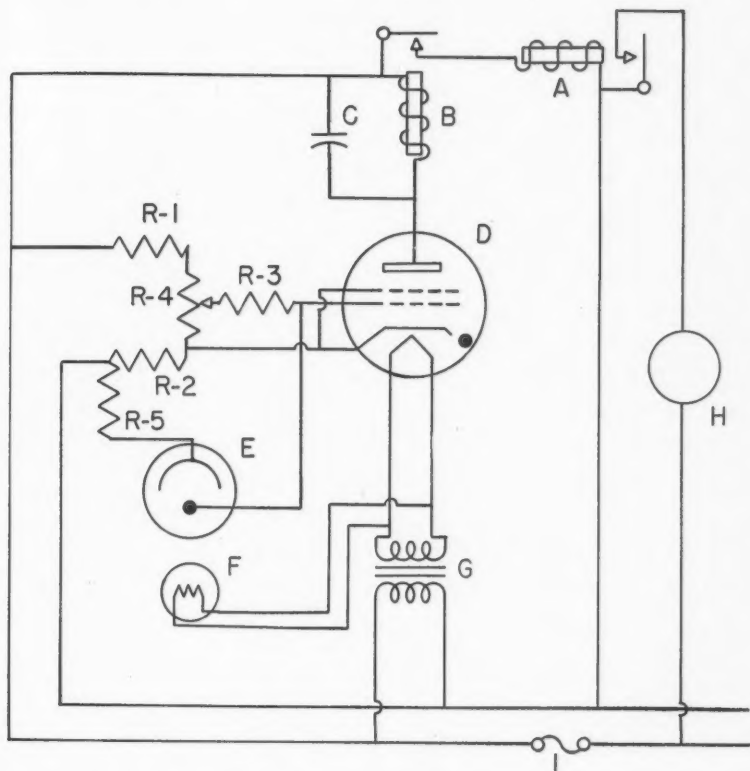


FIG. 2. Electronic relay circuit.

- A —normally open mercury relay  
coil: 115 v. 0.1 amp.  
contacts: 115 v. 30 amp.
- B —miniature relay  
coil: 115 v. 2 ma.  
contacts: 115 v. 2 amp.
- C —0.5  $\mu$ f. 200 v. condenser
- D —2050 amplifier tube
- E —Cetron CE-1-A/B photocell
- F —6 v. 1 amp. exciter lamp
- G —110 to 6 v. transformer
- H —vacuum pump motor or solenoid valve
- I —10 amp. fuse
- R-1—4000 ohm 5 w. resistor
- R-2—4000 ohm 1 w. resistor
- R-3—10 megohm max. resistor
- R-4—5000 ohm 1 w. resistor
- R-5—0.5 megohm min. resistor

The advantages of this device are (1) direct setting at the desired pressure, (2) continuous reading of pressure during operation, (3) elimination of metal to mercury contacts, and (4) ease of cleaning.

1. HUNTRESS, E. H. and HERSHBERG, E. B. *Ind. Eng. Chem., Anal. Ed.* 5: 144. 1933.
2. TODD, F. *Anal. Chem.* 20: 1249. 1948.

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